Stereocontrol during photo-initiated controlled/living radical polymerization of acrylamide in the presence of Lewis acids

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Poly(acrylamide) (PAM) with controlled molecular weight and tacticity was prepared by UV-irradiation-initiated controlled/living radical polymerization in the presence of dibenzyl trithiocarbonate (DBTTC) and $Y(OTf)_3$. The rapid and facile photo-initiated controlled/living polymerization at ambient temperature led to controlled molecular weight and narrow polydispersity (M_w/M_n = 1.12–1.24) of PAM. The coordination of $Y(OTf)_3$ with the last two amide groups in the growing chain radical effectively enhanced isotacticity of PAM. The isotactic sequence of dyads (*m*), triads (*mm*) and pentads (*mmmm*) in PAM were 70.32%, 50.95%, and 29.97%, respectively, which were determined by the resonance of methine (CH) groups in PAM under ^{13}C NMR experiment. Factors affecting stereocontrol during the polymerization were studied, including the type of Lewis acids, concentration of $Y(OTf)_3$, and monomer conversion. It is intriguing that the *meso* tacticity increased gradually with chain propagation and quite higher isotacticity (*m* = 93.01%, *mm* = 86.57%) was obtained in the later polymerization stage (conversion 65–85%).

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1. Introduction

The simultaneous control of molecular weight and tacticity of a polymer is one of the great challenges in controlled radical polymerization. For molecular weight control, controlled/living radical polymerization is the most useful procedure [1], with the following methods being widely employed: atom transfer radical polymerization (ATRP) [2,3]; nitroxide-mediated polymerization (NMP) [4–6]; and reversible addition–fragmentation chain transfer (RAFT) polymerization [7–9]. However, controlled/living radical polymerization has been much less successful in controlling tacticity and sequence distribution due to the radical nature of the propagation step [10]. In free-radical polymerization, the sp[2] hybridized carbon radical

has a nearly planar configuration, which offers similar probability of *meso* and *racemo* addition and therefore leads to atactic polymers.

Stereocontrol in free-radical polymerization of some acrylate derivatives has been achieved recently. Okamoto and Sato et al. reported a simple approach to increase the isotacticity of radical polymerization of acrylate derivatives, such as α-(alkoxymethyl)acrylates, methacrylates, di-*n*-butyl itaconate, methacrylamides, and acrylamide with the use of a Lewis acid [11–14]. The coordination of the Lewis acid with the last two segments of a growing polymer chain forces them into the *meso* configuration during the monomer addition and leads to an isotactic polymer [15].

The combination of stereocontrol and molecular weight control through controlled/living polymerization is a very tempting goal because it would enrich the macromolecular engineering tools and enable formation of new stereospecific polymers. Matyjaszewski [15] and Okamoto [16]

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studied ATRP polymerization and RAFT polymerization in the presence of Lewis acids, and both of them succeeded in obtaining stereospecific polymers with controlled molecular weights and narrow polydispersities. In contrast, the controlled/living polymerization they performed in a thermo-initiated polymerization system had a long polymerization period at high temperature.

Most recently, some methods of rapid and well-controlled living polymerization at ambient temperature have been proposed, and γ-irradiation [17–19], plasma irradiation [20], and UV-irradiation [21,22] have been successfully applied to activate or initiate controlled/living radical polymerization at ambient temperature. Of these, UV-irradiation is an easy and effective activation method for rapid and well-controlled living polymerization. We have applied UV-irradiation to initiate the controlled/living radical polymerization of acrylamide under the stereocontrol of a Lewis acid. Through the decomposition of the dibenzyl trithiocarbonate (DBTTC) into free radicals under UV-irradiation, the polymerization took place at ambient temperature in a relatively rapid manner.

In this article, PAM with controlled molecular weight and tacticity was prepared by a facile and rapid photo-initiated controlled/living polymerization under the chelate stereocontrol of a Lewis acid. More fine configurational sequences, including dyads, triads, and even pentads were determined by ^{13}C NMR resonance of the methine (CH) group instead of by ^{1}H NMR. Moreover, the dependence of tacticity of PAM and monomer conversion was investigated in detail, which revealed that the PAM obtained actually has a stereo gradient tacticity.

2. Experimental

2.1. Materials

Acrylamide (AM, 99%) was purchased from Shanghai Reagent Co. and recrystallized from ethyl acetate. Y(OTf)$_3$, Y(OAc)$_3$ and Y(MeSO$_3$)$_3$ were purchased from Aldrich and dried under vacuum just before use. Methanol was distilled over magnesium methoxide and stored over molecular sieves. Dibenzyl trithiocarbonate (DBTTC) was synthesized according to a previously published method [19].

A high pressure mercury vapor lamp (125W) with peak emissions at λ of 365 nm, which was purchased from Shanghai Yaming Lighting Co. Ltd., was used as a UV radiation source.

2.2. Polymerization

The polymerization of PAM was carried out in a sealed tube. The general procedure was as follows. AM, DBTTC, Y(OTf)$_3$ and methanol (monomer concentration of 4.5 M) were added into a tube and the mixture was stirred for 5 min at ambient temperature to give a clear solution. Then the solution was degassed by three freeze–evacuate–thaw cycles. The polymerization tube was sealed under vacuum conditions and then subjected to the UV

radiation for the prescribed time. The distance between the tube and the UV radiation source was kept at 10 cm. After the polymerization, the reaction mixture was diluted with water and then the solution was poured into a 10-fold excess of ethanol. The product was collected by filtration then dried in a vacuum oven. The conversion was calculated based on the following equation:

$$C\% = \frac{W_{PAM} - W_{DBTTC}}{W_{AM}} \times 100\%$$

where W_{PAM}, W_{DBTTC} and W_{AM} are the weights of the polymer obtained, DBTTC and the monomer added, respectively.

2.3. Characterization

The number-average molecular weights (M_n), weight-average molecular weights (M_w), and polydispersities (M_w/M_n) of the polyacrylamide (PAM) were determined by a PE 200 gel permeation chromatography (GPC) equipped with G6000 PW (XL) columns using poly(oxyethylene) as the calibration standard. An aqueous solution of NaNO$_3$ (0.01 M) was used as the effluent at a flow rate of 1.0 mL/min at 25 °C.

The ^{13}C NMR spectra were recorded on a Bruker WH 400 spectrometer. The samples were examined in 15% D$_2$O solutions at 70 °C at a pulse interval of 30 μs, and an acquisition time and pulse interval of 0.8 s were used. Relative peak areas were determined through curve resolution using Gaussian/Lorentzian peak shapes, and the assignment of the pentad sequence of methine (CH) lines was determined according to the literature [23,24]. The relationships of relative concentration between pentad and triad are known as [25]:

$$mmmm + mmmr + rmmr = mm$$
$$mmrm + mmrr + rmrm + rmrr = mr \qquad (1)$$
$$mrrm + mrrr + rrrr = rr$$

And then the relationships between triads and dyads are

$$mm + 0.5 \times mr = m \qquad (2)$$
$$rr + 0.5 \times mr = r$$

The number-average sequence length can be determined by the following equation:

$$N = 1/r$$
$$Nm = (mm + 0.5 \times mr)/(0.5 \times mr) \qquad (3)$$
$$Nr = (rr + 0.5 \times mr)/(0.5 \times mr)$$

where N, Nm, and Nr are the number-average sequence length of like configurations, *meso* and *racemic* addition, respectively.

3. Results and discussion

3.1. Controlled/living polymerization of AM under UV-irradiation

The monomer AM was polymerized under UV-irradiation at ambient temperature in the presence of DBTTC and Y(OTf)$_3$. In this system, Y(OTf)$_3$ was used as the chelate